Equilibrium Relationships between Oxide Compounds in MgO–Ti₂O₃–Al₂O₃ with Iron at 1 873 K and Variations in Stable Oxides with Temperature

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It is important to determine the equilibrium relationships between the oxide compounds in MgO–Ti₂O₃–Al₂O₃ and iron to avoid Al₂O₃ or MgO·Al₂O₃ formation and for inclusion control. In this study, the equilibrium relationships between the oxide compounds in MgO–Ti₂O₃–Al₂O₃ and molten iron are investigated at 1 873 K. The phase-stability diagrams, which show the equilibrium relationships between the oxide compounds in MgO–Ti₂O₃–Al₂O₃ and molten iron, are described. It is also important to know the oxides that newly form after solidification. Accordingly, the temperature-dependences of the stable compounds that newly form after solidification were investigated using the thermodynamic calculation software *FactSage 6.1*. Although the compounds formed after solidification are not necessarily the same as the equilibrium oxide compounds at 1 873 K, the correlation between them can be confirmed. In particular, under the unstable condition of MgAl₂O₄ at 1 873 K, it is found that the formation of MgAl₂O₄ could also be suppressed after solidification.

KEY WORDS: inclusion; deoxidation; equilibrium; oxide; iron; steelmaking.

1. Introduction

Nonmetallic inclusions in steel are mainly composed of deoxidation products, and they adversely affect the toughness, fatigability, and ductility of steel because of their high melting points and hardness. For example, it is very important to avoid the formation of Al₂O₃ and spinel (MgO·Al₂O₃) during the deoxidation of molten iron for high-grade wire and bearing steels. Several thermodynamic studies on the deoxidation equilibria of the Fe–Mg–Al–O and Fe–Ca–Mg–Al–O systems have been reported and the phase-equilibrium relationships between each oxide (or compound) and the composition of the solutes in molten iron have been clarified in the MgO–Al₂O₃ and CaO–MgO–Al₂O₃ systems.^{1–3)}

‘Oxide metallurgy’ is the control of inclusions and is used to improve the properties of steel.⁴⁾ The toughness of steel can be improved by finely dispersing nonmetallic inclusions in the steel and by causing the inclusions to act as nuclei for ferrite production in grains. Titanium oxide finely dispersed in steel and complex deoxidation involving titanium are considered to be effective for the above-mentioned purpose.⁵⁾ Determination of the equilibrium relationships between the oxide compounds in MgO–Al₂O₃–Ti₂O₃ and molten iron is important in avoiding Al₂O₃ or MgO·Al₂O₃ formation and for inclusion control.

In our previous work,⁶⁾ we reported the equilibrium relationships between the oxide compounds in MgO–Al₂O₃–

Ti₂O₃ and molten iron at 1 873 K. The formation of MgTi₂O₄ was confirmed as one of the equilibrium phases. However, there are insufficient thermodynamic data available on the formation of MgTi₂O₄. In this work, the equilibrium relationships between the oxide compounds in MgO–Ti₂O₃ and molten iron are investigated at 1 873 K, and the equilibrium constant of the formation of MgTi₂O₄ from magnesium, titanium, and oxygen in molten iron and the interaction parameter of Mg on Ti in iron are derived. Using the derived values, we describe the phase-stability diagrams, which show the equilibrium relationships between the oxide compounds in MgO–Ti₂O₃–Al₂O₃ and molten iron at 1 873 K. In inclusion control of steel, it is also important to know which oxides newly form after solidification. Accordingly, the variations in stable compounds with temperature are investigated using the thermodynamic calculation software *FactSage 6.1*.

2. Experimental

Ti₂O₃ was made using reagent grade TiO₂ (purity > 99%) and Ti (purity 98%) by mixing them in a molar ratio of 3:1. The mixture was put in an alumina crucible and the crucible was put in a carbon crucible with a lid and inserted in an electrical resistance furnace. The sample was held in the furnace for 18 h at 1 023 K under argon. After removal from the furnace, the compound was cooled under argon, and the formed Ti₂O₃ was then crushed to a powder before being

Table 1. Initial oxide compositions and metal contents after experiments at 1 873 K.

No.	Initial oxide compositions (mass%)		Metal contents [mass%]		
	Ti ₂ O ₃	MgO	Ti	Mg	O
1	70	30	0.130	0.0011	0.0012
2	60	40	0.069	0.0003	0.0009
3			0.046	0.0006	0.0011
4			0.069	0.0006	0.0011
5			0.087	0.0014	0.0022

Fig. 1. Schematic cross-section of a sample.

used for the following experiments.

We mixed the formed Ti₂O₃ powder and reagent grade MgO (purity > 99%) to obtain a total weight of 12 g. The initial compositions of the oxides are shown in **Table 1**. The mixture was put in an alumina crucible (O.D. 25 mm, I.D. 20 mm, height 35 mm), as shown in **Fig. 1**. High-purity electrolytic iron weighing about 6 g, which was deoxidized with H₂ at 1 873 K using an induction furnace, was then added to the mixture of oxides. The alumina crucible was put in a carbon crucible with a lid and was inserted in an electrical resistance furnace. The sample was heated to 1 273 K at a heating rate of 6.7 K/min under argon and then the temperature was maintained for 1 h. The sample was then heated to 1 873 K at a heating rate of 6.7 K/min under argon and kept at that temperature for 13 h. The sample was then removed from the furnace and cooled in an argon stream. After each experiment, the oxide compounds formed at the oxide/iron interface were identified by X-ray diffraction (XRD). The titanium and magnesium contents of the iron were analyzed by inductively coupled plasma (ICP) emission spectrometry. The oxygen content of the iron was analyzed by inert gas impulse infrared absorption spectroscopy. In order to suppress the effects of inclusion entrainment, the samples were analyzed more than twice for each element, and the content of each element was determined from the average of two or more analyzed values.

3. Results and Discussion

3.1. Experimental Results

The equilibrium relationships between the oxide compounds in MgO–Ti₂O₃ and molten iron were investigated at 1 873 K. XRD analysis was performed at the interface of the oxide and the iron after the experiments, and the results for samples No. 1 and No. 2 are shown in **Fig. 2**. The equilibrium phases were found to be MgO and MgTi₂O₄ for both samples. The equilibrium phases were also confirmed to be MgO and MgTi₂O₄ for the other samples. The dependences

Fig. 2. XRD patterns of samples No. 1 and No. 2. **Fig. 3.** Equilibrium phases plotted in the MgO–Al₂O₃–Ti₂O₃ diagram.

of the equilibrium phases on the initial composition of the oxides is shown in the MgO–Al₂O₃–Ti₂O₃ diagram in **Fig. 3**, together with previous results.⁶⁾ The titanium, magnesium, and oxygen contents of the molten iron for each sample are shown in Table 1. We found that the oxygen content was almost constant and that the magnesium content was low, in the range 3–14 mass ppm.

3.2. Equilibrium Relationships between the Oxide Compounds in MgO–Ti₂O₃ and Iron

In this work, the formation of MgTi₂O₄ is confirmed as one of the equilibrium phases. First, the equilibrium constant for the formation of MgTi₂O₄ from magnesium, titanium, and oxygen in molten iron, and the interaction parameter of Mg on Ti in iron at 1 873 K are derived. The reaction of MgTi₂O₄ with molten iron is expressed by Eq. (1). The equilibrium constant for Eq. (1) can be expressed by Eq. (2) using the interaction parameters and the solute concentration.

$$\begin{aligned} \log K_{(1)} &= \log(h_{\text{Mg}} \cdot h_{\text{Ti}}^2 \cdot h_{\text{O}}^4 / a_{\text{MgTi}_2\text{O}_4}) \\ &= \log f_{\text{Mg}} + \log [\% \text{Mg}] + 2 \log f_{\text{Ti}} + 2 \log [\% \text{Ti}] \\ &\quad + 4 \log f_{\text{O}} + 4 \log [\% \text{O}] = \log [\% \text{Mg}] + 2 \log [\% \text{Ti}] \\ &\quad + 4 \log [\% \text{O}] + (e_{\text{Mg}}^{\text{Ti}} + 2e_{\text{Ti}}^{\text{Ti}} + 4e_{\text{O}}^{\text{Ti}})[\% \text{Ti}] + (e_{\text{Mg}}^{\text{Mg}} + 2e_{\text{Ti}}^{\text{Mg}} \\ &\quad + 4e_{\text{O}}^{\text{Mg}})[\% \text{Mg}] + (e_{\text{Mg}}^{\text{O}} + 2e_{\text{Ti}}^{\text{O}} + 4e_{\text{O}}^{\text{O}})[\% \text{O}] \end{aligned} \dots\dots\dots (2)$$

a_i and h_i denote the activity of i relative to the pure solid and the activity of i relative to a 1 mass% dilute solution, respectively; $[\%i]$ denotes the concentration of component i in iron [mass%], f_i is the Henrian activity coefficient of component i relative to the dilute solution and e_i^j is the first-order interaction parameter of i on j in iron. The activity of MgTi_2O_4 , $a_{\text{MgTi}_2\text{O}_4}$ is unity, assuming the existence of a pure solid. In Eq. (2), the values for the interaction parameters are already known except $e_{\text{Ti}}^{\text{Mg}}$ and $e_{\text{Mg}}^{\text{Ti}}$. Equation (2) is rearranged by transposing $\log K_{(1)}$ and the terms including $e_{\text{Ti}}^{\text{Mg}}$ and $e_{\text{Mg}}^{\text{Ti}}$ to the right-hand side, and Eq. (4) is derived using Eq. (3), which is a conversion equation for the interaction parameters. M_i denotes the atomic weight of element i .

$$e_{\text{Ti}}^{\text{Mg}} = e_{\text{Mg}}^{\text{Ti}} (M_{\text{Ti}} / M_{\text{Mg}}) + 0.434 \times 10^{-2} \{ (M_{\text{Mg}} - M_{\text{Ti}}) / M_{\text{Mg}} \} \quad (3)$$

$$\begin{aligned} & \log[\% \text{Mg}] + 2 \log[\% \text{Ti}] + 4 \log[\% \text{O}] + (2e_{\text{Ti}}^{\text{Ti}} + 4e_{\text{O}}^{\text{Ti}})[\% \text{Ti}] \\ & + (e_{\text{Mg}}^{\text{Mg}} + 4e_{\text{O}}^{\text{Mg}})[\% \text{Mg}] + (e_{\text{Mg}}^{\text{O}} + 2e_{\text{Ti}}^{\text{O}} + 4e_{\text{O}}^{\text{O}})[\% \text{O}] \\ & + 2 \cdot 0.434 \times 10^{-2} \{ (24.3 - 47.9) / 24.3 \} [\% \text{Mg}] \\ & = -e_{\text{Mg}}^{\text{Ti}} ([\% \text{Ti}] + 2 \cdot 47.9 / 24.3 [\% \text{Mg}]) + \log K_{(1)} \end{aligned} \quad (4)$$

The values for the left-hand side of Eq. (4) can be determined by substituting each interaction parameter and the experimental results of each solute content of the molten iron. The thermodynamic data used in this work are shown in Table 2. In Fig. 4, the values for the left-hand side of Eq. (4) are plotted against $([\% \text{Ti}] + 2 \cdot \frac{47.9}{24.3} [\% \text{Mg}])$, in accordance with Eq. (4). From the intercept and the slope in Fig. 4, the values for $\log K_{(1)}$ and $e_{\text{Mg}}^{\text{Ti}}$ are determined as follows:

$$\log K_{(1)} = -18.7 (\pm 1.2) \quad (5)$$

$$e_{\text{Mg}}^{\text{Ti}} = -18.4 (\pm 13.2) \quad [e_{\text{Ti}}^{\text{Mg}} = -36.3 \text{ from Eq. (3)}] \quad (6)$$

Table 2. Mass percentage interaction parameters for Fe–Ti–Mg–Al–O at 1 873 K.

i	j	e_i^j	Reference
Ti	Ti	0.048	Janke <i>et al.</i> ⁽⁹⁾
	Al	0.0037	Yanchang <i>et al.</i> ⁽¹⁰⁾
	Mg	−36.3	Present work
	O	−1.619	Pak <i>et al.</i> ⁽⁷⁾
Al	Ti	0.004	Yanchang <i>et al.</i> ⁽¹⁰⁾
	Al	0.038	Satoh <i>et al.</i> ⁽¹¹⁾
	Mg	−0.13	Sigworth <i>et al.</i> ⁽⁸⁾
	O	−1.867	Satoh <i>et al.</i> ⁽¹¹⁾
Mg	Ti	−18.4	Present work
	Al	−0.12	Sigworth <i>et al.</i> ⁽⁸⁾
	Mg	−0.047	Satoh <i>et al.</i> ⁽¹¹⁾
	O	−0.602	Satoh <i>et al.</i> ⁽¹¹⁾
O	Ti	−0.541	Pak <i>et al.</i> ⁽⁷⁾
	Al	−1.105	Satoh <i>et al.</i> ⁽¹¹⁾
	Mg	−0.396	Satoh <i>et al.</i> ⁽¹¹⁾
	O	−0.175	Satoh <i>et al.</i> ⁽¹¹⁾

The standard error of the value for $e_{\text{Mg}}^{\text{Ti}}$ is rather large, and this is considered to be caused by the low Mg content of the molten steel.

The phase-stability diagram of MgTi_2O_4 , Ti_2O_3 , and MgO is derived from the following equilibrium constants for the reaction of each compound with molten iron.

$$\log K_{(1)} = -18.7 \text{ (at 1 873 K)} \quad (5)$$

$$\log K_{(7)} = -44\,238/T + 13.7 = -10.6 \text{ (at 1 873 K)} \quad (8)$$

$$\log K_{(9)} = -30\,760/T + 8.831^{(11)} = -7.59 \text{ (at 1 873 K)} \quad (10)$$

The equilibrium constants for Eqs. (7) and (9) are expressed by Eqs. (11) and (12), respectively, using the interaction parameters and the solute concentrations.

$$\begin{aligned} \log K_{(7)} &= \log(h_{\text{Ti}}^2 \cdot h_{\text{O}}^3 / a_{\text{Ti}_2\text{O}_3}) \\ &= 2 \log f_{\text{Ti}} + 2 \log[\% \text{Ti}] + 3 \log f_{\text{O}} + 3 \log[\% \text{O}] \\ &= 2 \log[\% \text{Ti}] + 3 \log[\% \text{O}] + (2e_{\text{Ti}}^{\text{Ti}} + 3e_{\text{O}}^{\text{Ti}})[\% \text{Ti}] \\ &+ (2e_{\text{Ti}}^{\text{Mg}} + 3e_{\text{O}}^{\text{Mg}})[\% \text{Mg}] + (2e_{\text{Ti}}^{\text{O}} + 3e_{\text{O}}^{\text{O}})[\% \text{O}] \end{aligned} \quad (11)$$

$$\begin{aligned} \log K_{(9)} &= \log(h_{\text{Mg}} \cdot h_{\text{O}} / a_{\text{MgO}}) \\ &= \log f_{\text{Mg}} + \log[\% \text{Mg}] + \log f_{\text{O}} + \log[\% \text{O}] \\ &= \log[\% \text{Mg}] + \log[\% \text{O}] + (e_{\text{Mg}}^{\text{Ti}} + e_{\text{O}}^{\text{Ti}})[\% \text{Ti}] \\ &+ (e_{\text{Mg}}^{\text{Mg}} + e_{\text{O}}^{\text{Mg}})[\% \text{Mg}] + (e_{\text{Mg}}^{\text{O}} + e_{\text{O}}^{\text{O}})[\% \text{O}] \end{aligned} \quad (12)$$

The doubly saturated curve with MgTi_2O_4 and Ti_2O_3 can be described by solving Eqs. (2) and (11), simultaneously. The thermodynamic data shown in Table 2 are used in the calculation. Similarly, the doubly saturated curve with MgTi_2O_4 and MgO can be described by solving Eqs. (2) and (12), simultaneously. The relationship between the Mg and Ti contents of the molten iron is shown in Fig. 5; the figure shows the stability regions of MgTi_2O_4 , MgO , and Ti_2O_3 at 1 873 K. The calculated iso-oxygen curve is shown in Fig. 5, and the experimental results are also plotted in Fig. 5. The numerical values in the figure show the experimental results for the oxygen content of molten iron [mass ppm O]. From

Fig. 4. Linear relationship of Eq. (4).

Fig. 5, it is found that the calculation is in reasonable agreement with the experimental results. As a titanium oxide that can be in equilibrium with molten iron, Ti_3O_5 is also generally considered under conditions of high oxygen content (or low titanium content). Here, the calculation is conducted for conditions under which Ti_3O_5 is not formed.

With respect to inclusion control of steel, it is also important to know which oxides newly form after solidification. Accordingly, variations in the stable compounds with temperature are investigated using the thermodynamic calculation software *FactSage 6.1*. The initial metal composition was determined from the phase-stability diagram described in this work, which is shown in Fig. 6. The initial metal composition is also shown in Table 3 with the calculation

Fig. 5. Stability regions of MgTi_2O_4 , MgO , and Ti_2O_3 at 1873 K.

Fig. 6. Initial metal compositions plotted on the stability diagram of the oxide compounds in $\text{MgO-Ti}_2\text{O}_3$ with molten iron at 1873 K.

conditions. Fact 53 and FSstel are used as the thermodynamic databases for pure substances and solutions, respectively. The equilibrium phase at 1873 K is MgO for Nos. ① and ②, MgTi_2O_4 for No. ③, and Ti_2O_3 for Nos. ④ and ⑤. The calculation was conducted at intervals of 50 K from 1673 K to 1873 K, and the temperature dependences of the newly formed stable compounds are shown in Figs. 7–9. In Fig. 7, the variations in the formed compounds with the initial composition (Ti and Mg contents) of the metal are compared at a fixed initial oxygen content of 15 mass ppm. The formation of titanium oxide (Ti_3O_5 or Ti_2O_3) is observed below 1773 K for each condition, and Ti_2O_3 begins to form at higher temperatures as the titanium content increases. For Nos. ③ and ④, the formation of the same compound as the equilibrium phase at 1873 K is confirmed. In contrast, for No. ①, the equilibrium phase at 1873 K is MgO , but the formation of MgO is not confirmed. Similarly, in Figs. 8 and 9, the variations in the formed compounds with the initial metal composition are compared at a fixed initial titanium content of 708 mass ppm and at a fixed initial magnesium content of 2.09 mass ppm, respectively. From Fig. 8, it is found that the formation of titanium oxide is prevented as the magnesium content increases, and in the case of No. ②, the formation of the same compound as the equilibrium phase at 1873 K, i.e., MgO , is confirmed after solidification. From Fig. 9, it is found that the formation of Mg_2TiO_4 is prevented and Ti_2O_3 begins to form at higher temperatures as the titanium content increases. In the case of No. ⑤, the formation of the same compound as the equilibrium phase at 1873 K, i.e., Ti_2O_3 , is confirmed after solidification. The validity of the thermodynamic data for the solutes in solid iron used for the above calculation cannot be verified. In this work, it is found that there is a strong affinity between Ti and Mg in molten iron. If this strong affinity is also present in solid iron, this suggests that Ti_2O_3 is easier to form than Mg_2TiO_4 in the above calculation.

3.3. Equilibrium Relationships between the Oxide Compounds in $\text{MgO-Al}_2\text{O}_3\text{-Ti}_2\text{O}_3$ and Iron

The phase-stability diagram of Ti_2O_3 , MgTi_2O_4 , and MgAl_2O_4 is derived from the following equilibrium constants for the reaction of each compound with molten iron.

$$\log K_{(1)} = -18.7 \text{ (at 1873 K)} \dots\dots\dots (5)$$

$$\log K_{(7)} = -10.6 \text{ (at 1873 K)} \dots\dots\dots (8)$$

Table 3. Initial metal compositions and calculation conditions for the equilibrium of oxide compounds in $\text{MgO-Ti}_2\text{O}_3$ and iron.

No.	Metal contents [mass ppm]			Databases	Solution species	Final Conditions		The equilibrium phase at 1873 K
	Ti	Mg	O			T [K]	P [atm]	
①	100	0.26	15	FSstel Fact 53	FSstel-FCC	1673–1873	1	MgO
②	708	55.6	1		FSstel-BCC			MgO
③	708	2.09	15		FSstel-FE-L			MgTi_2O_4
④	1030	0.26	15					Ti_2O_3
⑤	2430	2.09	10					Ti_2O_3

Fig. 7. Variations in the formed compounds with initial metal composition at a fixed initial oxygen content of 15 mass ppm.

Fig. 8. Variations in the formed compounds with initial metal composition at a fixed initial titanium content of 708 mass ppm.

$$\log K_{(13)} = 21.41 - 80980/T^{(8)} = -21.8 \text{ (at 1873 K)} \quad (14)$$

The equilibrium constants for Eqs. (1), (7), and (13) are expressed by Eqs. (15), (16), and (17), respectively, using the interaction parameters and the solute concentrations.

$$\begin{aligned} \log K_{(1)} &= \log(h_{\text{Mg}} \cdot h_{\text{Ti}}^2 \cdot h_{\text{O}}^4 / a_{\text{MgTi}_2\text{O}_4}) \\ &= \log f_{\text{Mg}} + \log[\% \text{Mg}] + 2 \log f_{\text{Ti}} + 2 \log[\% \text{Ti}] \\ &\quad + 4 \log f_{\text{O}} + 4 \log[\% \text{O}] = \log[\% \text{Mg}] + 2 \log[\% \text{Ti}] \\ &\quad + 4 \log[\% \text{O}] + (e_{\text{Mg}}^{\text{Ti}} + 2e_{\text{Ti}}^{\text{Ti}} + 4e_{\text{O}}^{\text{Ti}})[\% \text{Ti}] \\ &\quad + (e_{\text{Mg}}^{\text{Mg}} + 2e_{\text{Ti}}^{\text{Mg}} + 4e_{\text{O}}^{\text{Mg}})[\% \text{Mg}] + (e_{\text{Mg}}^{\text{Al}} + 2e_{\text{Ti}}^{\text{Al}} + 4e_{\text{O}}^{\text{Al}})[\% \text{Al}] \\ &\quad + (e_{\text{Mg}}^{\text{O}} + 2e_{\text{Ti}}^{\text{O}} + 4e_{\text{O}}^{\text{O}})[\% \text{O}] \end{aligned} \quad (15)$$

Fig. 9. Variations in the formed compounds with initial metal composition at a fixed initial magnesium content of 2.09 mass ppm.

$$\begin{aligned} \log K_{(7)} &= \log(h_{\text{Ti}}^2 \cdot h_{\text{O}}^3 / a_{\text{Ti}_2\text{O}_3}) \\ &= 2 \log f_{\text{Ti}} + 2 \log[\% \text{Ti}] + 3 \log f_{\text{O}} + 3 \log[\% \text{O}] \\ &= 2 \log[\% \text{Ti}] + 3 \log[\% \text{O}] + (2e_{\text{Ti}}^{\text{Ti}} + 3e_{\text{O}}^{\text{Ti}})[\% \text{Ti}] + (2e_{\text{Ti}}^{\text{Mg}} \\ &\quad + 3e_{\text{O}}^{\text{Mg}})[\% \text{Mg}] + (2e_{\text{Ti}}^{\text{Al}} + 3e_{\text{O}}^{\text{Al}})[\% \text{Al}] + (2e_{\text{Ti}}^{\text{O}} + 3e_{\text{O}}^{\text{O}})[\% \text{O}] \end{aligned} \quad (16)$$

$$\begin{aligned} \log K_{(13)} &= \log(h_{\text{Mg}} \cdot h_{\text{Al}}^2 \cdot h_{\text{O}}^4 / a_{\text{MgAl}_2\text{O}_4}) \\ &= \log f_{\text{Mg}} + \log[\% \text{Mg}] + 2 \log f_{\text{Al}} + 2 \log[\% \text{Al}] \\ &\quad + 4 \log f_{\text{O}} + 4 \log[\% \text{O}] = \log[\% \text{Mg}] + 2 \log[\% \text{Al}] \\ &\quad + 4 \log[\% \text{O}] + (e_{\text{Mg}}^{\text{Ti}} + 2e_{\text{Al}}^{\text{Ti}} + 4e_{\text{O}}^{\text{Ti}})[\% \text{Ti}] \\ &\quad + (e_{\text{Mg}}^{\text{Mg}} + 2e_{\text{Al}}^{\text{Mg}} + 4e_{\text{O}}^{\text{Mg}})[\% \text{Mg}] + (e_{\text{Mg}}^{\text{Al}} + 2e_{\text{Al}}^{\text{Al}} + 4e_{\text{O}}^{\text{Al}})[\% \text{Al}] \\ &\quad + (e_{\text{Mg}}^{\text{O}} + 2e_{\text{Al}}^{\text{O}} + 4e_{\text{O}}^{\text{O}})[\% \text{O}] \end{aligned} \quad (17)$$

The doubly saturated curve for Ti_2O_3 and MgTi_2O_4 can be obtained by solving Eqs. (15) and (16) simultaneously. Similarly, the doubly saturated curves for Ti_2O_3 and MgAl_2O_4 and MgTi_2O_4 and MgAl_2O_4 can be obtained by solving Eqs. (16) and (17) or Eqs. (15) and (17), respectively. The relationships among the four elements (Ti, Mg, Al, and O) in molten iron need to be considered. By fixing the content of one component, the relationships among the other three components can be determined from the two equilibrium equations. The relationship between the Al and Ti contents of molten iron was calculated at 1873 K using Eqs. (15)–(17) and the interaction parameters shown in Table 2. The phase-stability regions of MgTi_2O_4 , MgAl_2O_4 , and Ti_2O_3 when [mass ppm Mg] = 3 are shown in Fig. 10 together with our previous experimental results.⁶⁾ The numerical values near the open and closed circles show the oxygen content [mass ppm O]. The calculated iso-oxygen curves are also shown in Fig. 10. Overall, we found that the obtained experimental results are in reasonable agreement with the calculated results. When the titanium content of the molten iron is more than 0.1 mass%, Ti_2O_3 forms, and this is independent of the aluminum concentration. When the titanium con-

tent is less than 0.1 mass%, MgAl_2O_4 forms at Al mass% values above 0.003, and the region of MgAl_2O_4 formation widens as the titanium content of the molten iron decreases. It is necessary to lower the Al content to at least below Al mass% = 0.003 and to adjust the Ti content to within an appropriate concentration range so that MgTi_2O_4 can form when [mass ppm Mg] = 3.

As described in Section 4.1, the temperature dependences of the newly formed stable compounds are investigated using the thermodynamic calculation software *FactSage 6.1* for the equilibrium relationships between the oxide compounds in $\text{MgO-Ti}_2\text{O}_3\text{-Al}_2\text{O}_3$ and molten iron. The initial metal compositions were determined from the phase-stability diagram described in this work, as shown in **Fig. 11**. The initial metal compositions are also shown in **Table 4** with the calculation conditions. Fact 53 and FSstel are used as the thermodynamic databases for pure substances and solutions, respectively. The calculation was conducted at intervals of 50 K from 1 673 K to 1 873 K. The variations in the formed compounds with the initial composition (Ti and Mg contents) of the metal are compared in **Fig. 12** at a fixed initial oxygen content of 15 mass ppm. From **Fig. 12**, it is found that the formation of MgAl_2O_4 is prevented as the titanium content increases, and, for both No. 2 and No. 4, the formation of the same compound as the equilibrium phase at 1 873 K is confirmed after solidification. Moreover, in the case of No. 2, the formation of a complex oxide,

$(\text{FeO})_2(\text{TiO}_2)$, is confirmed. Similarly, in **Figs. 13** and **14**, the variations in the formed compounds with the initial metal composition are compared at a fixed initial titanium content of 168 mass ppm and at a fixed initial aluminum content of 6.68 mass ppm, respectively. From **Fig. 13**, it is found that MgAl_2O_4 forms with increasing aluminum content. From **Fig. 14**, it is found that the formation of MgAl_2O_4 is prevented and formation of Ti_2O_3 is confirmed as the titanium content increases. In cases No. 1 and No. 5, the formation of the same compound as the equilibrium phase at 1 873 K is confirmed after solidification. From these calculations, although the compound formed after solidification is not necessarily in accordance with the equilibrium oxide compound at 1 873 K, a correlation between them can be confirmed. In particular, formation of MgAl_2O_4 outside the stable region at 1 873 K is not confirmed. Under the unstable conditions for MgAl_2O_4 at 1 873 K in the phase-stability diagram shown in **Fig. 11**, it is found that the MgAl_2O_4 formation is also suppressed after solidification.

4. Conclusions

The equilibrium relationships between the oxide compounds in $\text{MgO-Ti}_2\text{O}_3\text{-Al}_2\text{O}_3$ and molten iron are investigated at 1 873 K. It is important to know which new oxides are formed after solidification. Accordingly, the variations

Fig. 10. Stability regions of MgTi_2O_4 , MgAl_2O_4 , and Ti_2O_3 at 1 873 K for [mass ppm Mg] = 3.

Fig. 11. Initial composition of metal plotted on the stability diagram of the oxide compounds in $\text{MgO-Ti}_2\text{O}_3\text{-Al}_2\text{O}_3$ with molten iron at 1 873 K when [mass ppm Mg] = 3.

Table 4. Initial metal compositions and calculation conditions for equilibrium of oxide compounds in $\text{MgO-Ti}_2\text{O}_3\text{-Al}_2\text{O}_3$ and iron.

No.	Metal contents [mass ppm]				Databases	Solution species	Final Conditions		The equilibrium phase at 1 873 K
	Ti	Mg	Al	O			T [K]	P [atm]	
[1]	10	3	6.68	10	FSstel Fact 53	FSstel-FCC FSstel-BCC FSstel-FE-L	1 673–1 873	1	MgAl_2O_4
[2]	10	3	2.99	15					MgAl_2O_4
[3]	168	3	39.4	5					MgAl_2O_4
[4]	168	3	0.75	15					MgAl_2O_4
[5]	2 450	3	6.68	10					Ti_2O_3

Fig. 12. Variations in the formed compounds with initial metal composition at a fixed initial oxygen content of 15 mass ppm.

Fig. 14. Variations in the formed compounds with initial metal composition at a fixed initial aluminum content of 6.68 mass ppm.

Fig. 13. Variations in the formed compounds with initial metal composition at a fixed initial titanium content of 168 mass ppm.

with temperature in the formed compounds after solidification are investigated using the thermodynamic calculation software *FactSage 6.1*. The conclusions are as follows.

(1) The equilibrium constant of the reaction of MgTi_2O_4 with molten iron and the interaction parameter of Mg on Ti at 1873 K are determined as follows:

$$\log K = -18.7 (\pm 1.2)$$

$$e_{\text{Mg}}^{\text{Ti}} = -18.4 (\pm 13.2)$$

(2) The phase-stability diagram, which show the equilibrium relationships between the oxide compounds in $\text{MgO-Ti}_2\text{O}_3\text{-Al}_2\text{O}_3$ and molten iron, is derived at 1873 K [mass ppm Mg] = 3. When the titanium content of the molten iron is more than 0.1 mass%, Ti_2O_3 forms, and this is independent of the aluminum concentration. When the titanium content is less than 0.1 mass%, MgAl_2O_4 forms at Al mass% values above 0.003 and the region of MgAl_2O_4 formation widens as the titanium content of the molten iron decreases.

(3) Although the compound formed after solidification is not necessarily in accordance with the equilibrium oxide compound at 1873 K, the correlation between them can be confirmed. In particular, under the unstable conditions for MgAl_2O_4 at 1873 K, it is found that its formation is suppressed after solidification.

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